OFFICE OF NAVAL RESEARCH

AD-A246 654

Technical Report No. 13

Molecular Recognition by O-BISDIEN and Its Dinuclear Complexes

by

Ramunas J. Motekaitis and Arthur E. Martell

Submitted to

DTIC
S ELECTE
FEB 2 4 1992
D
D

Inorganic Chemistry

Department of Chemistry
Texas A&M University
College Station TX 77843-3255

January 29, 1992

92-04223

92 2 18 140

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

EPORT SECURITY CLASSIFICATION Jnclassified	1b. RESTRICTIVE MARKINGS
ECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
IECLASSIFICATION/DOWNGRADING SCHEDULE	Distribution unlimited

RFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)

IAME OF PERFORMING ORGANIZATION Texas A&M Research Fdn.	6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research

IDDRESS (City, State, and ZIP Code) Box 3578 College Station TX 77843	7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington VA 22217

NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0451

ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington VA 22217	10 SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

TITLE (Include Security Classification)

Molecular Recognition by O-BISDIEN and Its Dinuclear Complexes

PERSONAL AUTHOR(S)
R. J. Motekaitis and A. E. Martell

TYPE OF REPORT Technical	13b TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) January 30, 1992	15 PAGE COUNT

SUPPLEMENTARY NOTATION

Submitted to Inorganic Chemistry

COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	O-BISDIEN, dinculear Cu(II)and Co(II) complexes, dioxygen complexes, malonic acid, phosphoric acid, glycine, acethydroxamic acid, potassium phorphorus formate, molecular recognition

ABSTRACT (Continue on reverse if necessary and identify by block number)

he protonated forms of the basic ligand 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane or [24]ane-N6O2)-BISDIEN) recognize certain anions. The compounds studied are malonic acid, phosphoric acid, glycine, cetohydroxamic acid, and potassium phosphonousformate in their various protonated and anionic forms. Detailed irmation constants measuring this recognition are reported for all species found. [24]ane-N6O2 also forms 1:1 and 1:2 jand to divalent transition metal ion complexes, with a variety of protonated species and one dinuclear hydroxo bridged irm. All of these cationic complexes of O-BISDIEN exhibit recognition toward the same substrates. The quantitative irmation constants for the species formed are also reported. Finally some kinetics are reported for both the formation and ecomposition of dioxygen complexes of selected O-BISDIEN-dicobalt-substrate systems and are discussed in light of rinciples of molecular recognition.

DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
a NAME OF RESPONSIBLE INDIVIDUAL Ronald D. De Marco	22b TELEPHONE (Include Area Code) (202) 696 5075	22c OFFICE SYMBOL

Molecular Recognition by O-BISDIEN and Its Dinuclear Complexes

Ramunas J. Motekaitis and Arthur E. Martell*

The protonated forms of the basic ligand 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetraco-sane or [24]ane-N6O2 (O-BISDIEN) recognize certain anions. The compounds studied are malonic acid, phosphoric acid, glycine, acetohydroxamic acid, and potassium phosphonousformate in their various protonated and anionic forms. Detailed formation constants measuring this recognition are reported for all species found. [24]ane-N6O2 also forms 1:1 and 1:2 ligand to divalent transition metal ion complexes, with a variety of protonated species and one dinuclear hydroxo bridged form. All of these cationic complexes of O-BISDIEN exhibit recognition toward the same substrates. The quantitative formation constants for the species formed are also reported. Finally some kinetics are reported for both the formation and decomposition of dioxygen complexes of selected O-BISDIEN-dicobalt-substrate systems and are discussed in light of principles of molecular recognition.

INTRODUCTION.

Chloride and bromide ions were found to coordinate in aqueous solution to protonated polyamine cryptands as early as 1975.[1] By nmr methods the stability of the H-bonded complex formed between an H_4L^{4+} and Cl^- was reported as 4.5 log units where L is a tight (2,2,2) cryptand. This compelx showed remarkable selectivity over that formed by the larger Br^- ion.[2] Since then many simple ions were studied by NMR to determine their recognition by various protonated polyamine cryptands.[3,4] Potentiometric methods were later introduced in order to make more accurate measurements and to help distinguish the more minor interactions with cryptands, in particular with O-BISTREN.[5-8]

O-BISDIEN, 1, the ligand of this study, is an H_6L macrocyclic ligand possessing a pair of diethylenetriamine moieties connected by means of two 5-atom diethyl ether bridges. It is capable of up to hexaprotonation and binuclear metal ion coordination. The binuclear centers have in turn been shown to bridge various molecules.[9-13] In related work several planar tetraamine macrocycles were studied for complexation with ATP.[14,15] In O-BISDIEN, the simplest example of bridge formation between two metal centers is the OH^- ion[16] which forms with great facility. Other examples of bridging studied in this laboratory are imidazolate, oxalato, mesoxalato, glycinato, catecholate, and 3.5-dilsulfocatecholate, which form with various stabilities with the various protonated forms of O-BISDIEN alone or with protonated mononuclear metal complexes or with its dinuclear complexes.[9-13,17] Even without metal ion involvement this macrocyclic ligand is remarkably capable in the recognition of negative substrates and can even catalyze hydrolytic reactions such as are illustrated in the work with ATP, AMP, and ADP and other negative anions with its tetra-, penta- and hexaprotonated forms.[18,19]

In the case when the metal ion is cobalt(II), an additional peroxide bridge forms under dioxygen concommittantly converting cobalt(II) to formally cobalt(III), 2. This latter system undergoes an electron rearrangement resulting in the net flow of electrons from the substrate to the peroxide resulting in oxidation involving the formation-regeneration of an intermediate cobalt(III)-cobalt(III) center. Such oxidation studies had been performied on oxalate, ketomalonate, catechols, and others are in progress.[10-13,17]

The purpose of the present work is to demonstrate this recognition-catalysis phenomenon by the introduction of various types of new bridges. While the emphasis is on recognition, for some systems this

paper also treats some rate measurements of oxidation in addition to complex formation between O-BISDIEN, cobalt, and ternary ligand in the presence and absence of dioxygen. These ligands are glycine, acetohydroxamic acid, potassium phosphonousformate and malonic acid.

Another related development is that O-BISDIEN has been shown to catalyze certain hydrolytic reactions and synthesis of polyphosphate groups.[20-23] Most other work on molecular recognition is being done in organic solvents and does not seem closely related to the present investigation.

EXPERIMENTAL

Potentiometric Titrations

All pH calibrations with standard dilute strong acid at 0.100 M ionic strength were performed in order to measure hydrogen ion concentration directly, hence the symbol containing brackets p[H] is used throughout to emphasize its meaning: $-\log_{10}[H^+]$.

Ligands Alone. A rather standardized procedure was followed for each prototropic substance.

Into a 100 mL jacketed-thermostated titration cell, equipped with p[H] and reference electrodes, fitted with inert gas (Argon) inlet-outlet and a 10 mL precision piston buret, were placed 5.000 mL of 1.000 M KCl (to set the ionic strength at 0.100) and a weighed quantity corresponding to 0.1 mmol of ligand and 45.00 mL distilled, degassed water. This makes 50.00 mL of an experimental solution containing 2.0×10^{-3} M ligand, which was then allowed to stand at least 1/2 hr at 25.0 °C. Pairs of p[H] vs mL 0.1027 M KOH added were recorded at equally spaced intervals at every 0.100 mL base until somewhat more base was added over that necessary to neutralize the titratable protons present on the ligand.

Acidification of amino acids and of salts of acids and back titration was achieved with 0.0941 M HCl.

Metal-Ligand Systems. Solutions were prepared as above except appropriate aliquots of standardized metal chloride solutions were added to achieve integral ratios of metal ion to ligand: 1:1, 1:2, and 1:3. The potentiometric equilibrium data were obtained as above, but more time was allowed for equilibrium.

Metal-Binary Ligand Systems. As described above, ~60 mg (0.1 mmol) of O-BISDIEN·6HBr was weighed directly and mixed with 0.1 mmol and 0.2 mmol metal ion and 0.10 mmol of the bridging ligand,

3

5.00 mL of 1.00 M KCl, and diluted to 50.00 mL with redistilled, degassed water. Some regions of the data collected required up to 15 min before recording.

Co(II) Systems Under O$_2$. Oxygen was introduced to O-BISDIEN Co(II) systems and titrated using 0.500 mL increments spaced at least 6 hr apart in order to reach an acceptable compromise between duration of the experiment and its accuracy.

Electronic Spectra

UV-VIS spectra were measured generally from 600-300 nm using a PE Model 553 Spectrophotometer equipped with a constant temperature cell compartment with a 1.000 cm quartz cell and pre-balanced with the pure reference electrolyte.

Kinetic measurements were followed in an apparatus consisting of a 1.000 cm quartz spectrophotometric flow cell connected through a peristaltic pump to a thermostated titration cell equipped with a Gilmont 2.000 mL precision burette for delivery of titrant, glass and reference electrodes, gas inlet for argon or oxygen and gas outlet tube, and stirred by means of a magnetic stirring bar.

RESULTS and DISCUSSION

Recognition of Malonic Acid

In preparation for the quantitative determination of the stability constants of malonate with the various protonated forms of O-BISDIEN very precise protonation constants were obtained for each substance separately under the conditions of the experiment. Hence for malonic acid, H$_2$Mal, its potentiometric curve was calculated back to a precision of 0.002 pH units using the two equilibria:

$$Mal + H^+ \rightleftharpoons HMal \qquad \log K_1^H = 5.269$$

$$HMal + H^+ \rightleftharpoons H_2Mal \qquad \log K_2^H = 2.625$$
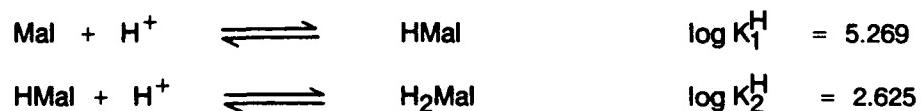
Similarly, the six log protonation constants for O-BISDIEN, Bd, which were found under the present experimental conditions and reproduce the titration curve within 0.003 p[H] units are:

$$Bd + H^+ \rightleftharpoons HBd \qquad \log K_1^H = 9.620$$

$$HBd + H^+ \rightleftharpoons H_2Bd \qquad \log K_2^H = 8.885$$

$$H_2Bd + H^+ \rightleftharpoons H_3Bd \qquad \log K_3^H = 8.285$$

$$H_3Bd + H^+ \rightleftharpoons H_4Bd \qquad \log K_4^H = 7.618$$

4

$$H_4Bd + H^+ \rightleftharpoons H_5Bd \qquad \log K_5^H = 3.815$$

$$H_5Bd + H^+ \rightleftharpoons H_6Bd \qquad \log K_6^H = 3.301$$
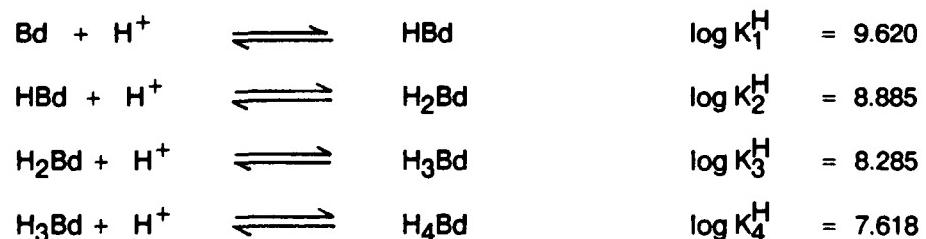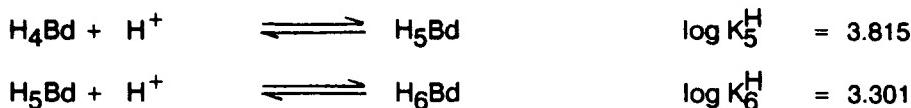
With the above values of individual protonation constants, the solution data on O-BISDIEN containing an equimolar quantity of malonic acid were resolved showing the presence of six equilibrium species:

$$H_6Bd^{6+} + HMal^- \rightleftharpoons H_7BdMal^{5+} \qquad \log K_7^R = 2.2\,(1)$$

$$H_6Bd^{6+} + Mal^{2-} \rightleftharpoons H_6BdMal^{4+} \qquad \log K_6^R = 4.2\,(1)$$

$$H_5Bd^{5+} + Mal^{2-} \rightleftharpoons H_5BdMal^{3+} \qquad \log K_5^R = 3.70(6)$$

$$H_4Bd^{4+} + Mal^{2-} \rightleftharpoons H_4BdMal^{2+} \qquad \log K_4^R = 2.38(6)$$

$$H_3Bd^{3+} + Mal^{2-} \rightleftharpoons H_3BdMal^{+} \qquad \log K_3^R = 2.05(4)$$

$$H_2Bd^{2+} + Mal^{2-} \rightleftharpoons H_2BdMal \qquad \log K_2^R = 1.81(8)$$
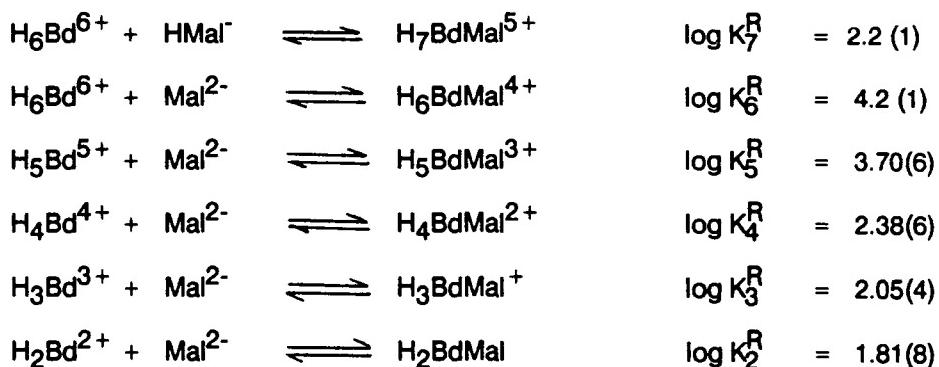
where K_i^R is the recognition constant of protonation degree i and the entries are listed in order of appearance from low to high p[H]. Possible H-bonding for the most stable of these species, $H_6(BD)Mal^{4+}$, is illustratd by formula 3.

As the degree of protonation on Bd increases, its affinity for Mal^{2-} increases as measured by the magnitude of K_i^R. But there are other factors which determine the relative concentrations of these variously protonated ternary complexes. Figure 1 shows that just as p[H] determines the state of protonation of the Bd molecule it also determines the degree of protonation of the substrate. At p[H] values up to 2 Bd is in its hexaprotonated state and malonate is practically all H_2Mal. Obviously, there could be no interaction between the two major species. Gradually, as the p[H] is increased, H_2Mal dissociates producing a significant concentration of $HMal^-$ which readily combines with the high concentration of H_6Bd^{6+} to form the initial ternary complex H_7BdMal^{5+}. At p[H] 3.6 $HMal^-$ as well as H_5Bd^{5+} reach their maximum concentration favoring the formation of H_6BdMal^{4+}. Similarly, near p[H], 4.6 Mal^{2-} starts forming while H_5Bd^{5+} reaches its maximum concentration, favoring the formation of H_5BdMal^{3+}. Beyond p[H] 5.3 there are no more protonated forms of malonic acid and hence the relative concentrations of the recognition complexes at their respective maxima decrease with p[H]. While the greatest observed concentration favors the symmetrical H_4BdMal^{2+} structure, intrinsically it is the H_6BdMal^{4+} complex which is the most stable, but it barely exceeds 9 % formation because of strong proton competition. On the

other hand, HBdMal⁻ probably is too weak to measure at these concentrations. While it may appear quite remarkable how strong the recognition of Mal^{2-} can be, it should be borne in mind that there is not only a favorable topological relationship between these ions leading to strong, possibly linear hydrogen bonds, but also a very favorable coulombic factor.

Other dinegative ligands which have been studied by these authors are mesoxalic acid and oxalic acid and their results are compared with this work in Table 1. There is no question that ketomalonate is till the strongest recognized substrate of all the entries in the Table 1. Since the keto group is highly hydrated, this unusual interaction is probably helped by additional hydrogen bonding to the ether bridging oxygens of O-BISDIEN. In contrast the malonate methylene is considerably hydrophobic and is probably not as well accommodated in this solvated environment. Oxalate is shorter and considerably more acidic, but O-BISDIEN is also very flexible. The Catechols possess extremely weak, monodentate aromatic hydroxy groups and are therefore not capable of forming a complex at low p[H] where they are neutral. At high⁻ p[H] where they are at least in part dissociated, but the macrocycle is devoid of protons under these conditions and does not H-bond to the catecholate.

Other O-BISDIEN Guests.

As part of the survey of a diverse family of potential guests, glycine, acetohydroxamic acid, phosphonousformic acid and phosphoric acid were considered for study. It was found that both glycine and acetohydroxamic acid do not interact significantly with the protonated forms of O-BISDIEN. Their log protonation constants were redetermined and found to be 9.58, 2.36 for glycine and 9.28 for the hydroxamate. The lack of strong recognition is explained by these high protonation constants and the magnitude of the protonation constants for O-BISDIEN. Thus by the time the p[H] is raised to 9.6 or 9.3 respectively to get 1/2 of the guest molecules deprotonated, the O-BISDIEN distribution consists of the unreactive forms: 1/2 Bd free base, 1/4 HBd^+, and 1/4 H_2Bd^{2+}, and hence becomes very uninviting to the mononegative ligands. However for acetohydroxamic acid the following three species were identified: H_7BdAcx^{6+}, H_6BdAcx^{5+}, H_5BdAcx^{4+} with corresponding log overall constants of formation of 54.05, 50.25, and 45.82 respectively.

Phosphonousformic acid proved to be too unstable in acid solution to study its interactions with O-BISDIEN although its log protonation constants were determined via a fast back titration from its dipotassium salt to be 3.19 and 1.7. However at low and even intermediate p[H] values the solutions drift because of autodecomposition so that the required precise measurements for interactions with the protonated forms of the macrocycle were deemed not possible although it is certain by analogy that such interactions should take place.

Phosphate is a smaller anion and judging from its log protonation constants (11.74, 6.75, and 1.72) only species $H_2PO_4^-$ and HPO_4^{2-} are important between p[H] 2 and 10. However six species were formed with O-BISDIEN to the extent that depends on the solution p[H] and the magnitudes of the protonation constant as summarized in the following equations:

$$H_6Bd^{6+} + H_2PO_4^- \rightleftharpoons H_8BdPO_4^{5+} \qquad \log K_8^R = 2.66(5)$$

$$H_6Bd^{6+} + HPO_4^{2-} \rightleftharpoons H_7BdPO_4^{4+} \qquad \log K_7^R = 6.97(3)$$

$$H_5Bd^{5+} + HPO_4^{2-} \rightleftharpoons H_6BdPO_4^{3+} \qquad \log K_6^R = 5.2 (1)$$

$$H_4Bd^{4+} + HPO_4^{2-} \rightleftharpoons H_5BdPO_4^{2+} \qquad \log K_5^R = 2.6 (1)$$

$$H_3Bd^{3+} + HPO_4^{2-} \rightleftharpoons H_4BdPO_4^{1+} \qquad \log K_4^R = 1.85(7)$$

$$H_2Bd^{2+} + HPO_4^{2-} \rightleftharpoons H_3BdPO_4^0 \qquad \log K_3^R = 1.49(7)$$
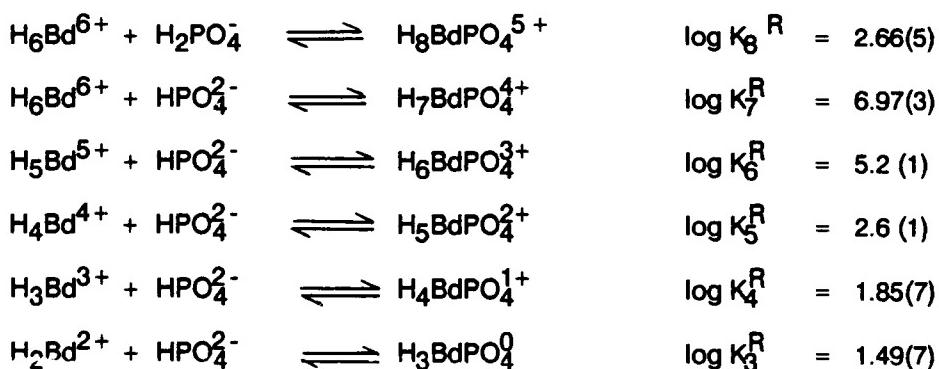
It is clear that the two most favored recognition equilibria involve the interaction of the hexa- and pentaprotonated O-BISDIEN molecule with the dinegative biphosphate. Not only is stability achieved through coulombic attraction but the phosphate molecule possesses at least 3 sites for hydrogen bond formation. Also the remaining site has a proton which is capable of formation of a fourth hydrogen bond. The remaining 4 interactions are weaker for differing reasons. $H_8BdPO_4^{5+}$ forms in a weaker fashion because of the mononegative $H_2PO_4^-$ ion. The ion $H_5BdPO_4^{2+}$ is more reluctant to form for geometric reasons. So whatever destabilizes $H_5BdPO_4^{2+}$ also then destabilizes $H_4BdPO_4^{1+}$ and $H_3BdPO_4^0$, which have fewer hydrogens for hydrogen bonding.

Figure 2 is interesting in that is shows phosphate-O-BISDIEN the species formed as a function of p[H]. The relative concentration of the 7-, 6-, and 5-protonated complexes at first appears out of order relative to the decreasing magnitude of the corresponding recognition constants. One would expect

$H_5BdPO_4^{2+}$ to have a much lower concentration. However note that we are above p[H] 6.75, the value corresponding to the protonation constant of HPO_4^{2-}, which means that the actual concentration of HPO_4^{2-} is changing from the negligible to finite-and-large values. Thus even though the log K^R_5 = 2.64 is small, the concentration conditions are very favorable for its (i.e. $H_5BdPO_4^{2+}$) formation. Note that the extents of formation of $H_4BdPO_4^{1+}$ and H_3BdPO_4 are indeed controlled by their small equilibrium constants and by the lessened concentration of any individual overlapping protonated form of O-BISDIEN present.

Copper-O-BISDIEN-Phosphate

Divalent metal ions, and in particular Cu(II), had already been shown to form both 1:1 and 1:2 ligand to metal complexes with O-BISDIEN: $CuBd^{2+}$, $CuH_{-1}Bd^+$, $CuHBd^{3+}$, CuH_2Bd^{4+}, CuH_3Bd^{5+}, Cu_2Bd^{4+}, $Cu_2H_{-1}Bd^{3+}$ and $Cu_2H_{-2}Bd^{2+}$. Mononuclear complex formation is favored when 1:1 ligand to metal ion solutions are prepared and dinuclear complexes are favored in 1:2 ligand to metal overall stoichiometry. Thus for both 1:1 and 1:2 ligand to metal ratios, the p[H] profiles obtained in the presence of phosphate show that the following interactions are significant:

$$CuH_3Bd^{5+} + H_2PO_4^- \rightleftharpoons CuH_5BdPO_4^{4+} \qquad \log K^R_{15} = 2.0\,(4)$$

$$CuH_3Bd^{5+} + HPO_4^{2-} \rightleftharpoons CuH_4BdPO_4^{3+} \qquad \log K^R_{14} = 6.45(6)$$

$$CuH_2Bd^{4+} + HPO_4^{2-} \rightleftharpoons CuH_3BdPO_4^{2+} \qquad \log K^R_{13} = 4.11(5)$$

$$CuHBd^{3+} + HPO_4^{2-} \rightleftharpoons CuH_2BdPO_4^+ \qquad \log K^R_{12} = 3.3\,(2)$$

$$CuBd^{2+} + HPO_4^{2-} \rightleftharpoons CuHBdPO_4^0 \qquad \log K^R_{11} = 2.8\,(2)$$

$$Cu_2Bd^{4+} + HPO_4^{2-} \rightleftharpoons Cu_2HBdPO_4^{2+} \qquad \log K^R_{21} = 4.5\,(2)$$
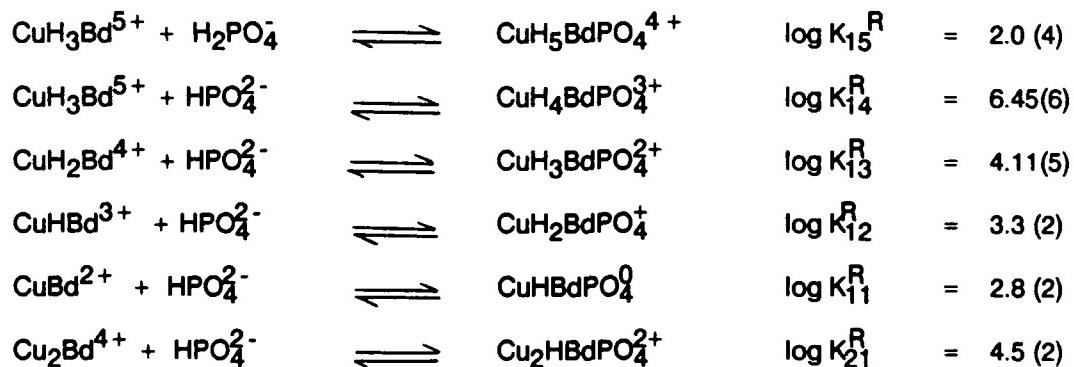
Only six of the 8 O-BISDIEN Copper(II) complexes possess recognition characteristics for phosphate. $CuH_{-1}Bd^+$ and $Cu_2H_{-2}Bd^{2+}$ are self-explanatory in their lack of reactivity. The inertness of $Cu_2H_{-1}Bd^{3+}$ can be appreciated when one recalls that the Cu_2Bd^{4+} ion has very high affinity for the OH^- ion, much higher than phosphate can compete with.

$$Cu_2Bd^{4+} + OH^- \rightleftharpoons Cu_2(OH)Bd^{3+} \qquad \log K^{OH} = 7.27$$

The species possessing the highest recognition constant for HPO_4^{2-} is CuH_3Bd^{5+}, 4, while the lowest is $CuBd^{2+}$ with decreasing values in between as the number of positive protons decreases. Once

again, HPO_4^{2-} not only possesses high charge but also has structural properties (tetrahedral symmetry) naturally fitting into the space between the protonated diethylenetriamine moiety and the metal ion to which it can coordinate. Even when the nitrogens aren't quaternized, the HPO_4^{2-} ion can coordinate to the Cu^{2+} ion as well as it can hydrogen bond to the covalent H atoms on the neutral nitrogens. The reason log K^R_{11} is 2.8 and is less than that of the Cu^{2+} reaction with HPO_4^{2-} (3.3) is related the energy required to unfold a part of O-BISDIEN during the transformation of $CuBd^{2+}$ into $CuHBdPO_4^0$, 5. No such unfolding is necessary in the case of Cu^{2+} ion. The log K^R_{15} is only 2.0, but note that it is a dihydrogen phosphate which is crowding itself into CuH_3L^{5+} to give $CuH_5BdPO_4^{4+}$, a species possessing a diprotonated bridging group.

Figures 3 and 4 show the various phosphate interactions discussed above for 1:1:1 and 1:1:2 O-BISDIEN to phosphate to copper(II) respectively. Only the phosphate-containing species are shown. In the mononuclear system, almost the entire p[H] range shows substantial concentrations of coordinated phosphate. In the dinuclear system, above p[H] ~9, the aforementioned dinuclear M-hydroxo species eventually displaces all of the phosphate.

Cobalt-O-BISDIEN-Malonate

Although Co^{2+} is a weak complexor for carboxylic acids, its affinity for malonate was redetermined under the conditions of this work. Two stability constants were found and their values are compared in Table 2 with the other ligands measured. Note that the numerical value

$$Mal^{2-} + Co^{2+} \rightleftharpoons CoMal \qquad \log K_{ML} = 2.92$$

$$Mal^{2-} + CoMal \rightleftharpoons Co(Mal)_2^{2-} \qquad \log K_{ML} = 1.68$$
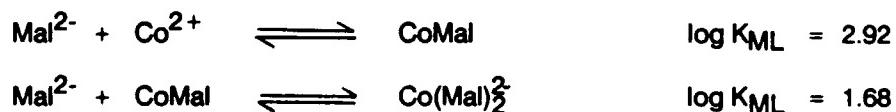
is two orders of magnitude smaller for the cobalt(II) complex compared to the affinity of the proton. Log K_{ML} for O-BISDIEN with Co^{2+} was found to be 9.81 (KCl) which is in good agreement with previous work (9.73) in KNO_3 as a supporting electrolyte. In a certain sense, all the constants discussed are somewhat dependent on the background electrolyte in that specific anion interactions from the background electrolyte were not factored out. In this work, an M_2L complex was not detected, although previous work (KNO_3) found a value of 2.7. In this work it was fortunately possible to reach a = 6.5 so that a numerical

constant was evaluated for the formation of $Co_2L(OH)^{3+}$ before cobalt hydroxide separated as was the case in the previous study.

$$2Co^{2+} + Bd \rightleftharpoons Co_2Bd(OH)^{3+} + H^+ \quad Log\, \beta = 4.50$$
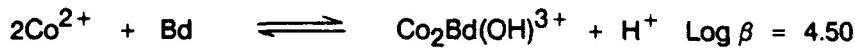
The two protonated complexes MHL^{3+} and MH_2L^{4+} were also found to form.

$$CoBd + H^+ \rightleftharpoons MHL^{3+} \qquad Log\, K^H_{MHL} = 7.37$$

$$CoHBd^{3+} + H^+ \rightleftharpoons MH_2L^{4+} \qquad Log\, K^H_{MHL} = 6.27$$
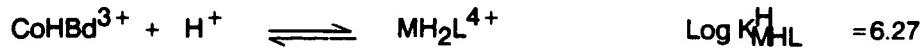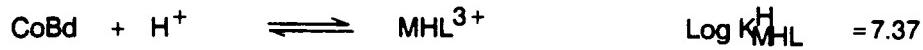
The differences between these values and those in the literature are attributable to the different salts used as background electrolyte.

Of the four Co(II)-BISDIEN complexes listed in Table 2, three showed some degree of molecular recognition for malonate ions to produce five species: $CoHBdMal^+$, CoH_2BdMal^{2+}, CoH_3BdMal^{3+}, $Co_2H_{-1}BdMal^+$ and Co_2BdMal^{2+}. The equilibrium expressions are:

$$CoHBd^{3+} + Mal^{2-} \rightleftharpoons CoHBdMal^+ \qquad log\, K^R_{11} = 3.15(8)$$

$$CoH_2Bd^{4+} + Mal^{2-} \rightleftharpoons CoH_2BdMal^{2+} \qquad log\, K^R_{12} = 3.39(6)$$

$$CoH_2Bd^{5+} + HMal^- \rightleftharpoons CoH_3BdMal^{3+} \qquad log\, K^R_{13} = 4.7\,(1)$$

$$Co_2H_{-1}Bd^{3+} + Mal^{2-} \rightleftharpoons Co_2H_{-1}BdMal^+ \qquad log\, K^R_2 = 3.1\,(2)$$

$$Co_2H_{-1}Bd^{3+} + Mal^{2-} \rightleftharpoons Co_2BdMal^{2+} + OH^- \qquad log\, K^R_{20} = -2.2\,(1)$$
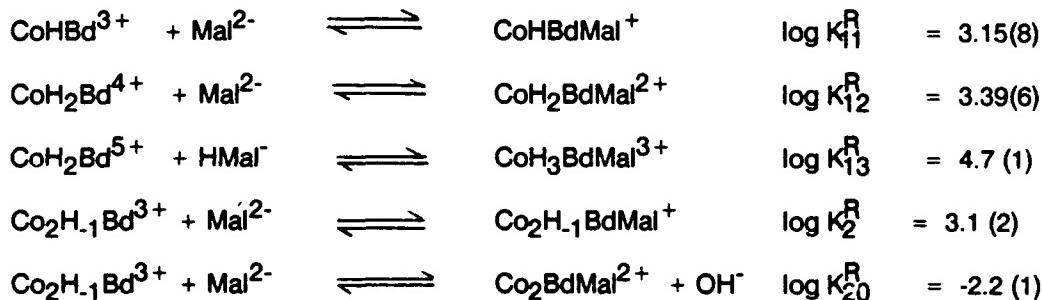
The equilibria symbolized by $log\, K^R_{11}$ and $log\, K^R_{12}$ are in stepwise order and thus increase slightly with the additional proton. The equilibrium symbolized by $log\, K^R_{13}$ is written in terms of a reaction with monohydrogen malonate since CoH_3Bd^{6+} does not exist. Nevertheless the recognition constant $log\, K^R_{13}$ is grater than $log\, K^R_{12}$. The first binuclear (μ-hydroxo) complex forms a malonato bridged species in contrast to the observations of the dicopper phosphate system discussed above. Note that all of the recognition constants in the above block of equations are greater in magnitude than the normal stability constant of Co^{2+} with Mal^{2-}. Formation of bridges over several centers is consistent with the observed magnitudes of constants. The recognition constant $log\, K^R_{20} = -2.16$ is written as an OH^- displacement reaction and it is considered remarkable that malonate is only 2 orders of magnitude disfavored over a hydroxo bridge, thus making it possible to observe this species before the p[H] gets too high. Figure 5

illustrates the p[H] dependence of the various O-BISDIEN/Co(II) malonato adducts discussed in this section.

A different p[H] profile is obtained for the O-BISDIEN, Co(II)-malonate system when it is carried out in the presence of dioxygen. From the differences, two equilibrium constants leading to the formation of $Co_2BdMal(O_2)^{2+}$ and $Co_2(OH^-)BdMal(O2)^+$ were obtained to reproduce the new curve. The equilibration is very slow and hence takes several days to get the necessary points in the dioxygen region.

$$\log \frac{[Co_2BdMal(O_2)^{2+}]}{[Co^{2+}]^2[Bd][Mal^{2-}]P_{O_2}} = 19.6(1)$$

$$\log \frac{[Co_2(OH^-)BdMal(O_2)^{2+}][H^+]}{[Co^{2+}]^2[Bd][Mal^{2-}]P_{O_2}} = 12.9(1)$$

In Figure 6, the dioxygen complexes are plainly obvious, especially the non-hydroxo-bridged $Co_2BdMal(O_2)^{2+}$, 6, where apparently the malonato bridge has displaced the hydroxo bridge and is the only major species near p[H] 6.

Cobalt-O-BISDIEN-Glycinate

Whereas the malonate stability constants of cobalt(II) are small, three stepwise reactions occur with glycinate and in addition a hydrolysis reaction was determiend.

$$Gly^- + Co^{2+} \rightleftharpoons CoGly^+ \qquad \log K_{ML} = 4.67(1)$$

$$Gly^- + CoGly^+ \rightleftharpoons Co(Gly)_2 \qquad \log K_{ML_2} = 3.81(1)$$

$$Gly^- + Co(Gly)_2 \rightleftharpoons Co(Gly)_3^- \qquad \log K_{ML_3} = 2.36(1)$$

$$CoGly^+ \rightleftharpoons CoGly(OH) + H^+ \qquad \log K^{OH} = -10.09(1)$$

The magnitude of these constants is such that a millimolar 1:3 cobalt to glycine solution would completely coordinate cobalt by p[H] 9. This certainly could not be said of malonic acid.

When O-BISDIEN is studied under argon with cobalt(II) and glycine, four new molecular recognition equilibrium species are identified, of which three are major while the last one is minor. $Co(OH)BdGly$, $CoHBdGly^{2+}$, $Co2Bd(Gly)_2^{2+}$ and Co_2BdGly^{3+}.

$$\frac{[Co^{2+}(OH)BdGly^-][H^+]}{[Co^{2+}][Bd][Gly^-]} = 10^{4.33}$$

$$\frac{[CoHBdGly^{2+}]}{[Co][Bd][Gly^-][H^+]} = 10^{21.94}$$

$$\frac{[Co_2Bd(Gly)_2^{2+}]}{[Co^{2+}]^2[Bd][Gly^-]^2} = 10^{21.58}$$

$$\frac{[Co_2BdGly^{3+}]}{[Co^{2+}]^2[Bd][Gly^-]} = 10^{16.57}$$

The second quotient may be rewritten into a more intuitive form using the overall $CoHBd^{3+}$ formation constant.

$$CoHBd^{3+} + Gly^- \rightleftharpoons CoHBdGly^{2+} \qquad \log K_1^R = 4.8$$

This recognition constant is slightly higher than the normal stability constant of the cobalt ion therefore showing the participation of the protonated nitrogen in some sort of H-bonding. In comparing the last two quotients one can write an equation for the addition of a second glycinate to one that is already there.

$$Co_2BdGly^{3+} + Gly^- \rightleftharpoons Co_2Bd(Gly)_2^{2+} \qquad \log K_2^R = 5.0$$
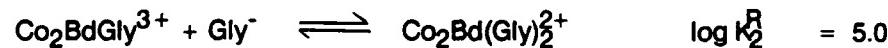
This constant is even higher than that of the first glycinate, and it would seem logical that this molecule involves the presence of two glycinato bridges between the cobalts.

Figure 7 shows the weak recognition that O-BISDIEN-Cobalt complexes exhibit for the monoanionic glycinate ligand. Most of the remaining glycine concentration is distributed among the various cobalt complexes that are formed (see Table 2).

Under oxygen, there are found three glycine-containing O-BISDIEN-Cobalt-Dioxygen complexes which actually swamp those formed from dicobalt-O-BISTREN alone. Their stoichiometries are: $Co_2Bd(OH)Gly(O_2)^{2+}$, 7, $Co_2BdH_{-2}Gly(O_2)^+$, and $Co_2BdH_{-3}Gly(O_2)$. The first complex is the expected one; however the last two probably involve replacements of coordinated neutral nitrogens for negative OH^-s. Their overall stability constants are as follows.

$$\log \frac{[Co_2(OH^-)BdGly(O_2)^{2+}][H^+]}{[Co^{2+}]^2[Bd][Gly^-]P_{O_2}} = 16.1(1)$$

12

$$\log \frac{[Co_2(H_{-2})BdGly(O_2)^{2+}][H^+]^2}{[Co]^2[Bd][Gly^-]P_{O_2}} = 7.5(1)$$

$$\log \frac{[Co_2(H_{-3})BdGly(O_2)^{2+}][H^+]^3}{[Co]^2[Bd][Gly^-]P_{O_2}} = -2.1(1)$$

These can be directly compared when expressed as Gly^- reacting with bisdiendicobalt dioxygen complexes.

$$Co_2Bd(OH)(O_2)^{3+} + Gly^- \rightleftharpoons Co_2Bd(OH)Gly(O_2)^{2+} \quad \log K = 7.0$$

$$Co_2BdH_{-2}(O_2)^{2+} + Gly^- \rightleftharpoons Co_2BdH_{-2}Gly(O_2)^+ \quad \log K = 6.6$$

$$Co_2BdH_{-3}(O_2)^+ + Gly^- \rightleftharpoons Co_2BdH_{-3}Gly(O_2) \quad \log K = 6.3$$

The fact that the values decrease means that the glycinate is more weakly bound to the dinuclear cobalt macrocyclic complexes as the number of coordinated OH^- ions increases. Figure 8 illustrates the formation of the three dioxygen complexes starting at p[H] 5.75 and going higher.

Cobalt-O-BISDIEN-Acetohydroxamate.

Acetohydroxamic acid possesses a basicity similar to that of glycine except it is monobasic and is not dipolar. That's why it's not surprising that its 1:1,1:2, and 1:3 stability constants are found to be very similar to those of glycine.

$$Acx^- + Co^{2+} \rightleftharpoons CoAcx^+ \quad \log K_{ML} = 4.99(1)$$

$$Acx^- + CoAcx^+ \rightleftharpoons Co(Acx)_2 \quad \log K_{ML_2} = 3.92(1)$$

$$Acx^- + Co(Acx)_2 \rightleftharpoons Co(Acx)_3 \quad \log K_{ML_3} = 2.66(1)$$
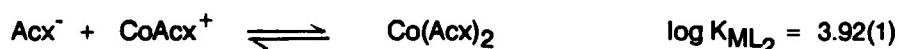
In the presence of O-BISDIEN, only two mixed ligand species were identified: $CoBdAcx^+$ and $Co_2Bd(Acx)_2^{2+}$ and their overall stability constants were found to be: 14.66 and 22.82 log units respectively. It is informative to re-express the formation of the mononuclear complex as a reaction with Acx^-.

$$CoBd^{2+} + Acx^- \rightleftharpoons CoBdAcx^+ \quad \log K^R = 4.93$$

13

Note once again the more favorable recognition constant than the normal stability constant for the Co^{2+} ion alone. It should be recalled that there are hydrogen bondable protons on the macrocycle nitrogens, and hydrogen bonds are probably involved in the binding of hydroxamate within the macrocycle.

A p[H] profile was attempted under dioxygen, but computations could not be carried out since the p[H] never stabilized enough to determine even approximate constants.

Cobalt-O-BISDIEN-Dioxygen Complex Kinetics

Table 3 is a summary of the rate constants obtained where possible for typical formation and degradation reactions of encapsulated dioxygen complexes. In Table 3, the k_{obs} was computed for the formation from original spectrophotometric data typical sample is shown in Figure 9 which depicts successive spectra obtained every 2 min when 1 O-BISDIEN, 2 Co(II), and 1 Glycine (1 millimolar) are mixed and heated at 45 °C. From a plot of $\log_e(A_\infty - A_t)$ vs time the slope was set equal to k_{obs}.

Degradation reactions were treated similarly from data obtained from series of spectra similar to the malonato decomposition curve shown in Figure 10 at 55 °C. Since the degradation was much slower than the formation reaction, it was possible to separate the kinetics of the degradation reaction which were all run under 1.0 atm of dioxygen.

A detailed investigation of any of the reaction products was not attempted, but there is no reason to assume otherwise than what had been learned in our earlier studies of oxalic acid and mesoxalic acid as substrates as well as preliminary findings in the catechol studies. In all of theses cases a discrete substrate-dioxygen complex adduct serves as an intermediate electron sink toward facilitation of electron flow from the reducing bridging substrate to the coordinated dioxygen, which was reduced to water.

14

REFERENCES

1. Graf, E.; Lehn, J. M. *J. Am. Chem. Soc.*, **1975** *97*, 5022.

2. Graf, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 6405.

3. Lehn, J. M.; Sonveaux, E.; Willard, A.K. *J. Am. Chem. Soc.* **1978**, *100*, 4194.

4. Dietrich, B.; Guilhem, J.; Lehn, J. M.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91.

5. Motekaitis, R. J.; Martell, A. E.; Lehn, J. M.; E. I. Watanabe, *Inorg. Chem.* **1982**, *21*, 4253.

6. Motekaitis, R. J. ;Martell, A. E.; Dietrich, B.; Lehn, J. M. *Inorg. Chem.* **1984**, *23*, 1588.

7. Motekaitis, R. J.; Martell, A. E.; Murase, I. *Inorg. Chem.* **1986**, *25*, 938.

8. Heyer, D.; Lehn, J. M. *Tetrahedron Lett.* **1986**, *27*, 5869.

9. Motekaitis, R. J.; Martell, A. E.; Lecomte, J. P.; Lehn, J. M. *Inorg. Chem.* **1983**, *22*, 609.

10. Martell A. E.; Motekaitis, R. J. *J. Chem. Soc. Chem. Commun.* **1988**, 915.

11. Martell, A. E.; Motekaitis, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8059.

12. Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 694.

13. Martell, A. E.; Motekaitis, R. J. In: *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Ed. Simandi, L. I.; Elsevier: Amsterdam, **1991**; pp.331-336.

14. Merecek, J. F.; Burrows, C.J. *Tetrahedron Lett.* **1986**, *27* 5943.

15. Merecek, J. F.; Fischer, P.A.; Burrows, C.J. *Tetrahedron Lett.* **1988**, *29*, 6231.

16. Coughlin , P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328.

17. Martell, A. E. *J. Inclus. Phenomena* **1988**, *7*, 99.

18. Hosseini, M. W.; Lehn, J. M.; Mertes, M. *Helv.Chim. Acta* **1983**, *66*, 2454.

19. Hosseini, M. W. ; Lehn, J. M. *Helv. Chim. Acta* **1987**, *70*, 1312.

20. Hosseini, M. W.; Lehn, J. M.; Jones, K. *J. Am. Chem. Soc.* **1989**, *111*, 6330.

21. Hosseini, M. W.; Lehn, J. M.; Maggiora, L. *J. Am. Chem. Soc.* **1989**, *109*, 537 and references cited therein.

22. Hosseini, M.W.; Lehn, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7047.

23. Hosseini, M.W.; Blacker, A.J.; Lehn, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 3896 and references cited therein.

Table 1. Log Host Formation Constants With Protonated Forms of O-BISDIEN

Ion	$\log K_1^H$	$\log K_2^H$	$\log K_i^R$'s					
			6	5	4	3	2	1
Malonate	5.27	2.63	4.2	3.70	2.38	2.05	1.81	
Ketomalonate	3.52	1.82	5.15	4.52	3.65	4.16	3.83	3.39
Oxalate	3.38	1.0	4.68	3.59	2.06			
Catecholate	13.3	9.30	none					
Tironate	12.5	7.62	none					

Table 2. Measured Formation Constants of H(I) and Co(II) With Ligands.

Quotient	Malonic Acid	Glycine	Acetohydro-xamic Acid	Phosphonous-formate	O-BISDIEN
$\dfrac{[HL]}{[H][L]}$	5.27	9.58	9.28	3.19	9.62
$\dfrac{[H_2L]}{[H][HL]}$	2.62	2.36	-	1.7	8.89
$\dfrac{[H_3L]}{[H][H_2L]}$	-	-	-	-	8.2
$\dfrac{[H_4L]}{[H][H_3L]}$	-	-	-	-	7.62
$\dfrac{[H_5L]}{[H][H_4L]}$	-	-	-	-	3.82
$\dfrac{[H_6L]}{[H][H_5L]}$	-	-	-	-	3.30
$\dfrac{[ML]}{[M][L]}$	2.92	4.67	4.99	-	9.81
$\dfrac{[ML_2]}{[L][ML]}$	1.68	3.81	3.92	-	-
$\dfrac{[ML_3]}{[L][ML_2]}$	0.7	2.36	2.66	-	-
$\dfrac{[MLOH][H]}{[ML]}$	-	10.09	-	-	-
$\dfrac{[M_2L(OH)][H]}{[M]^2[L]}$	-	-	-	-	4.50
$\dfrac{[MHL]}{[H][ML]}$	-	-	-	-	7.37
$\dfrac{[MH_2L]}{[H][MHL]}$	-	-	-	-	6.27

Table 3. Rate Constants Determined in This Investigation from Visible Spectra of Dicobalt(II) Dioxygen Band

Process	System	K_{obs}	Temp, °C
Formation	Bd-O$_2$	1.6×10^{-3}	45
Formation	Bd-Acx-O$_2$	1.0×10^{-3}	45
Formation	Bd-Pf-O$_2$	1.3×10^{-3}	45
Formation	Bd-Mal-O$_2$	9.5×10^{-4}	45
Decomposition	Bd-O$_2$	9.4×10^{-6}	45
Decomposition	Bd-Acx-O$_2$	9.4×10^{-6}	45
Decomposition	Bd-Gly-O$_2$	9.4×10^{-6}	45
Decomposition	Bd-Pf-O$_2$	9.4×10^{-6}	45
Decomposition	Bd-Pf-O$_2$	2.6×10^{-5}	25
Decomposition	Bd-Mal-O$_2$	2.3×10^{-5}	35

FIGURE CAPTIONS

Figure 1. Species distribution diagram showing the species formed as a function of p[H] when 2.09 $\times 10^{-3}$ M 1:1 O-BISDIEN (Bd) and Malonic Acid (H_2Ma) are equilibrated at 25.0 °C, μ = 0.100 M KCl.

Figure 2. Species distribution diagram showing the species formed as a function of p[H] when 2.02 $\times 10^{-3}$ M 1:1 O-BISDIEN (Bd) and 1.96 $\times 10^{-3}$ M Phospate (H_3P) are equilibrated at 25.0 °C, μ = 0.100 M KCl.

Figure 3. Species distribution diagram showing the species formed as a function of p[H] when 2.08 $\times 10^{-3}$ M 1:1:1 O-BISDIEN (Bd), 2.12 $\times 10^{-3}$ M Phospate (H_3P), and 2.08 $\times 10^{-3}$ M Copper(II) are equilibrated at 25.0 °C, μ = 0.100 M KCl. Only phosphate containing species are shown.

Figure 4. Species distribution diagram showing the species formed as a function of p[H] when 2.02 $\times 10^{-3}$ M 1:1:2 O-BISDIEN (Bd), 1.96 $\times 10^{-3}$ M Phospate (H_3P), and 3.90 $\times 10^{-3}$ M Copper(II) are equilibrated at 25.0 °C, μ = 0.100 M KCl. Only phosphate containing species are shown.

Figure 5. Species distribution diagram showing the species formed as a function of p[H] when 2.11 $\times 10^{-3}$ M 1:1:2 O-BISDIEN (Bd), 2.11 $\times 10^{-3}$ M Malonate (H_2Ma), and 4.20 $\times 10^{-3}$ M Cobalt(II) are equilibrated at 25.0 °C, μ = 0.100 M KCl. Only malonate containing complex species are shown.

Figure 6. Species distribution diagram showing only the dioxygen containing species formed as a function of p[H] when 2.13 $\times 10^{-3}$ M 1:1:2 O-BISDIEN (Bd), 2.11 $\times 10^{-3}$ M Malonate (H_2Ma), and 4.25 $\times 10^{-3}$ M Cobalt(II) are equilibrated at 25.0 °C, μ = 0.100 M KCl. There are 37 species considered in the background of this calculation. P_{O2} = 1.00 Atm.

Figure 7. Species distribution diagram showing the species formed as a function of p[H] when 1.99 $\times 10^{-3}$ M 1:1:2 O-BISDIEN (Bd), 2.04 $\times 10^{-3}$ M glycine (Gl), and 4.03 $\times 10^{-3}$ M cobalt(II) are equilibrated at 25.0 °C, μ = 0.100 M KCl. Only glycine containing complex species are shown.

Figure 8.   Species distribution diagram showing only the dioxygen containing species formed as a

function of p[H] when 1.92×10^{-3} M 1:1:2 O-BISDIEN (Bd), 1.92×10^{-3} M glycine (Gl), and

3.81×10^{-3} M cobalt(II) are equilibrated at 25.0 °C, $\mu = 0.100$ M KCl. There are 35 species

considered in the background of this calculation. $P_{O2} = 1.00$ Atm.

Figure 9.   Electronic spectra scanned every 2 min apart showing the formation of the

biscobaltbisdien-μ-hydroxo-μ-glycinato-μ-dioxygen complex at 6×10^{-4} M concentration.

Absorbance plotted against nanometers using 1.00 cm quartz cell, $\mu = 0.100$ M KCl at 45.0

°C. This is a typical formation curve before decomposition sets in.

Figure 10.   Electronic spectra scanned every 15 min apart showing the decomposition of the

biscobaltbisdien-μ-hydrixo-μ-malonato-μ-dioxygen complex at 6×10^{-4} M concentration.

Absorbance plotted against nanometers using 1.00 cm quartz cell, $\mu = 0.100$ M KCl at 45.0

°C. This is a typical set of degradation curves eventually leading to a featureless inert

Co(III) spectrum at infinite time.

Figure 1
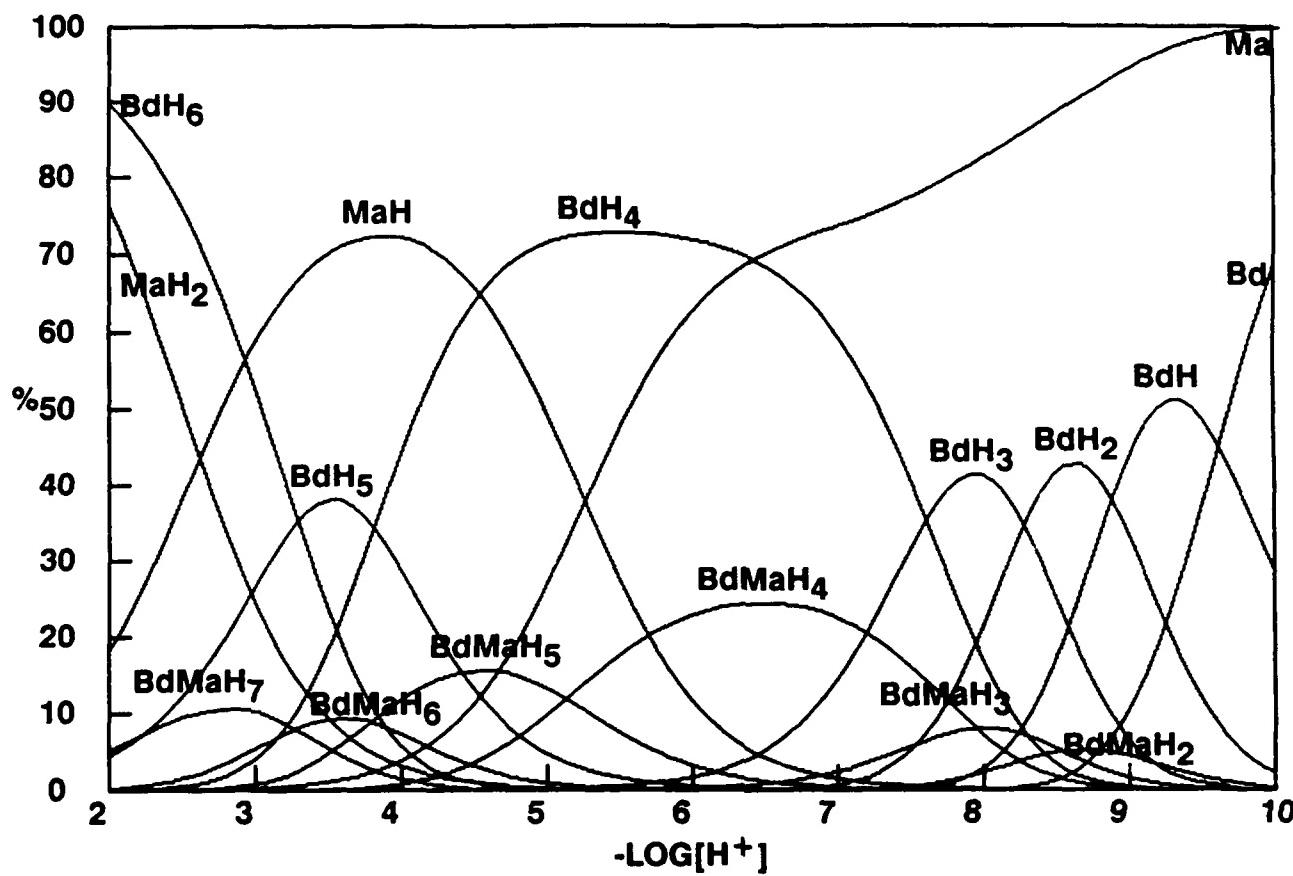
Figure 1
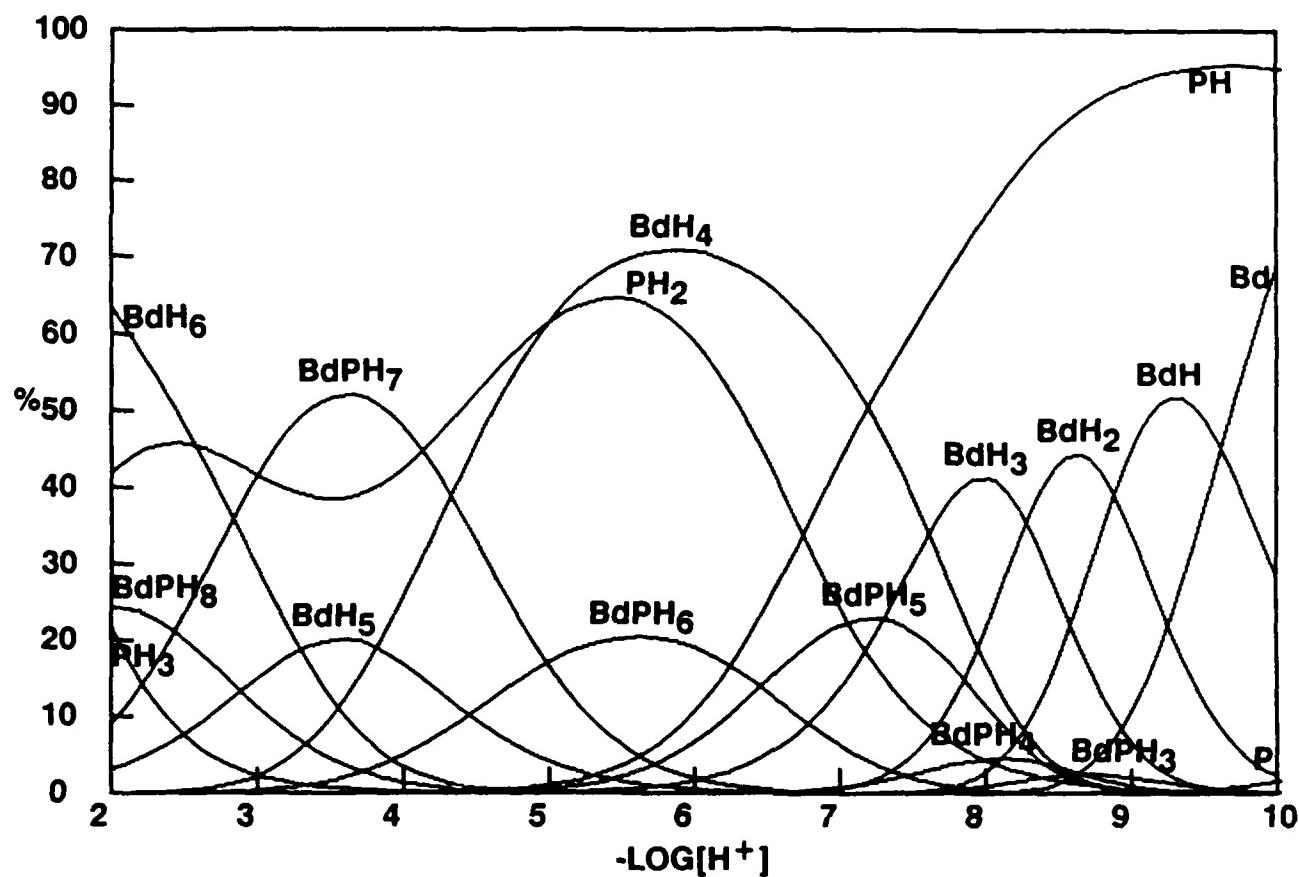
Figure 2

Figure 2
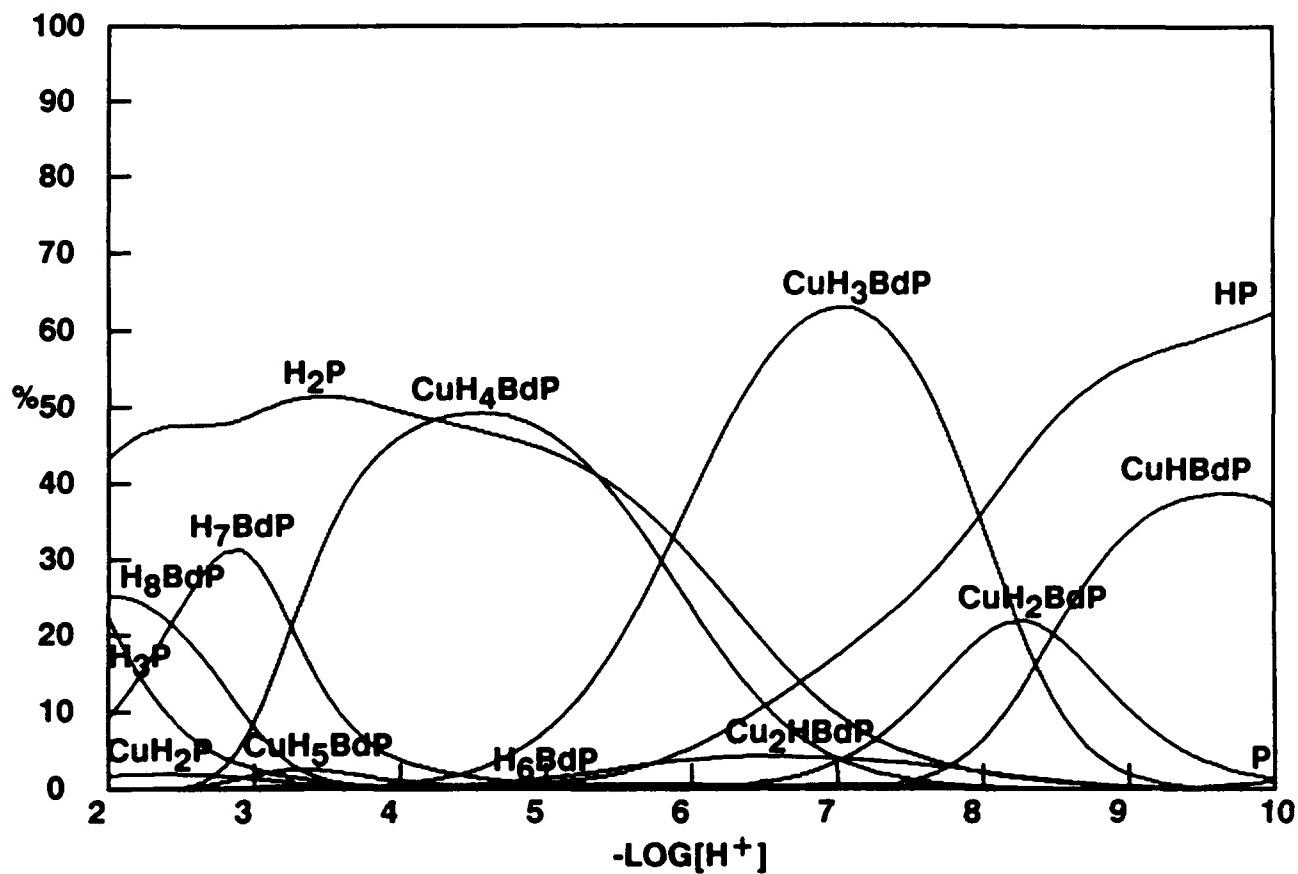
Figure 3

Figure 4
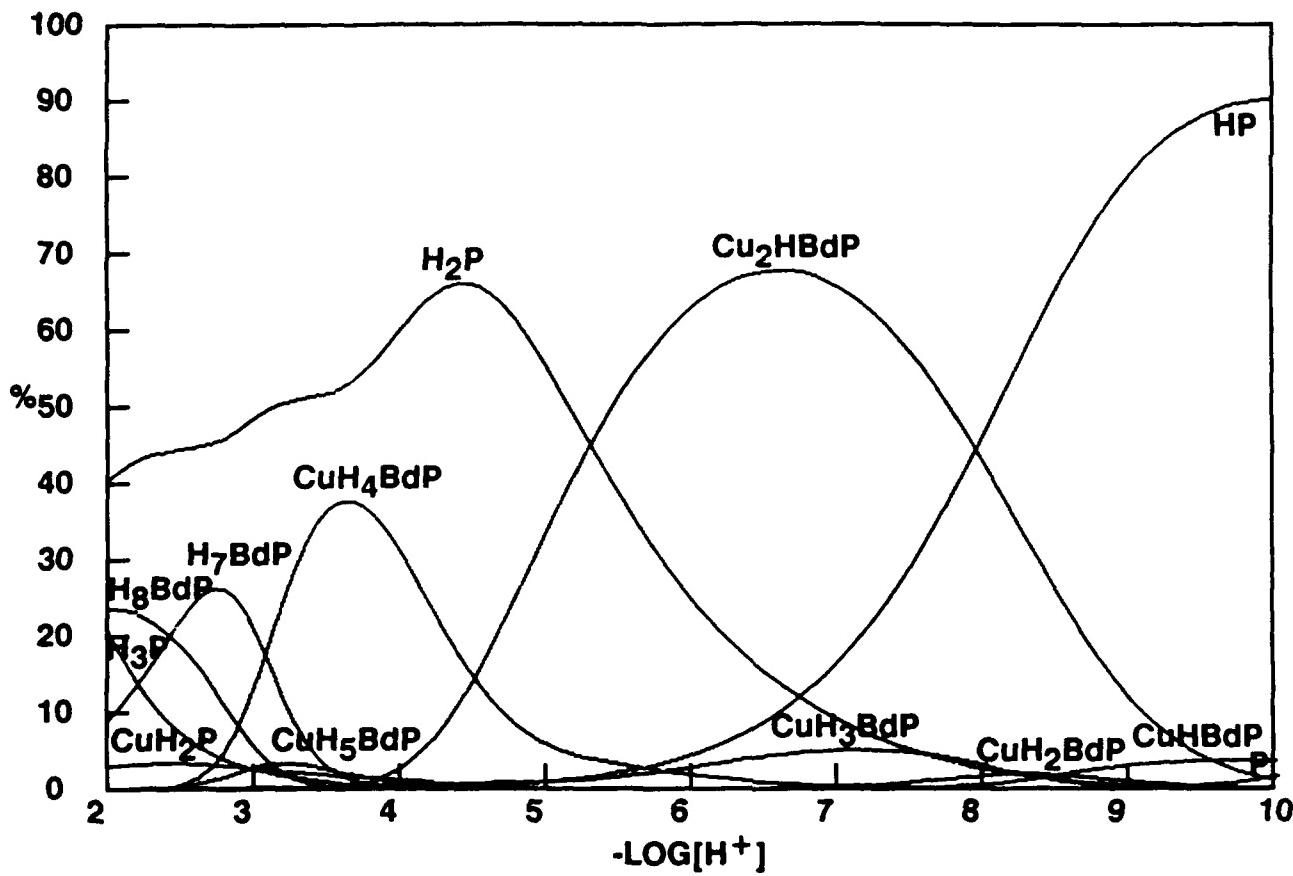
Figure 4
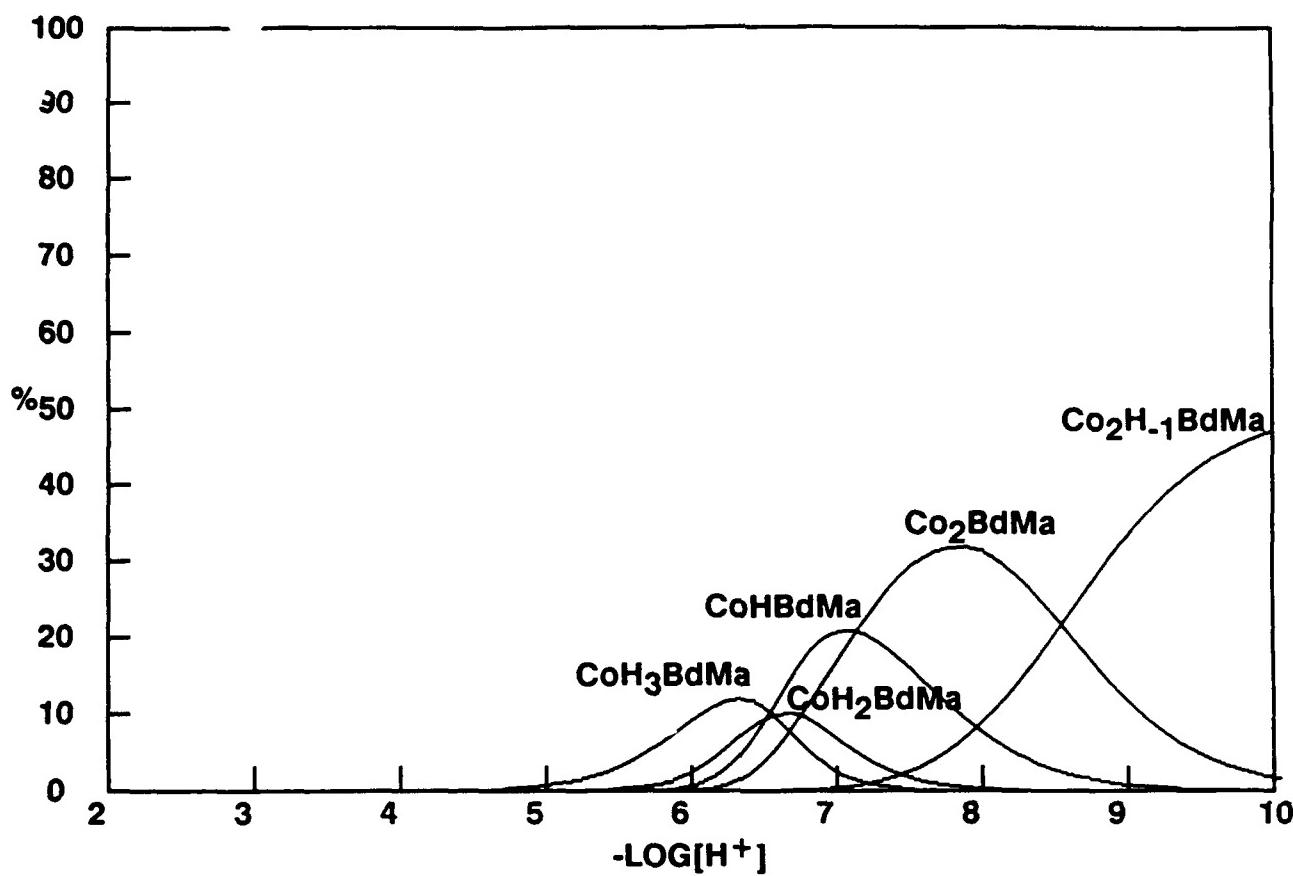
Figure 5

Figure 6
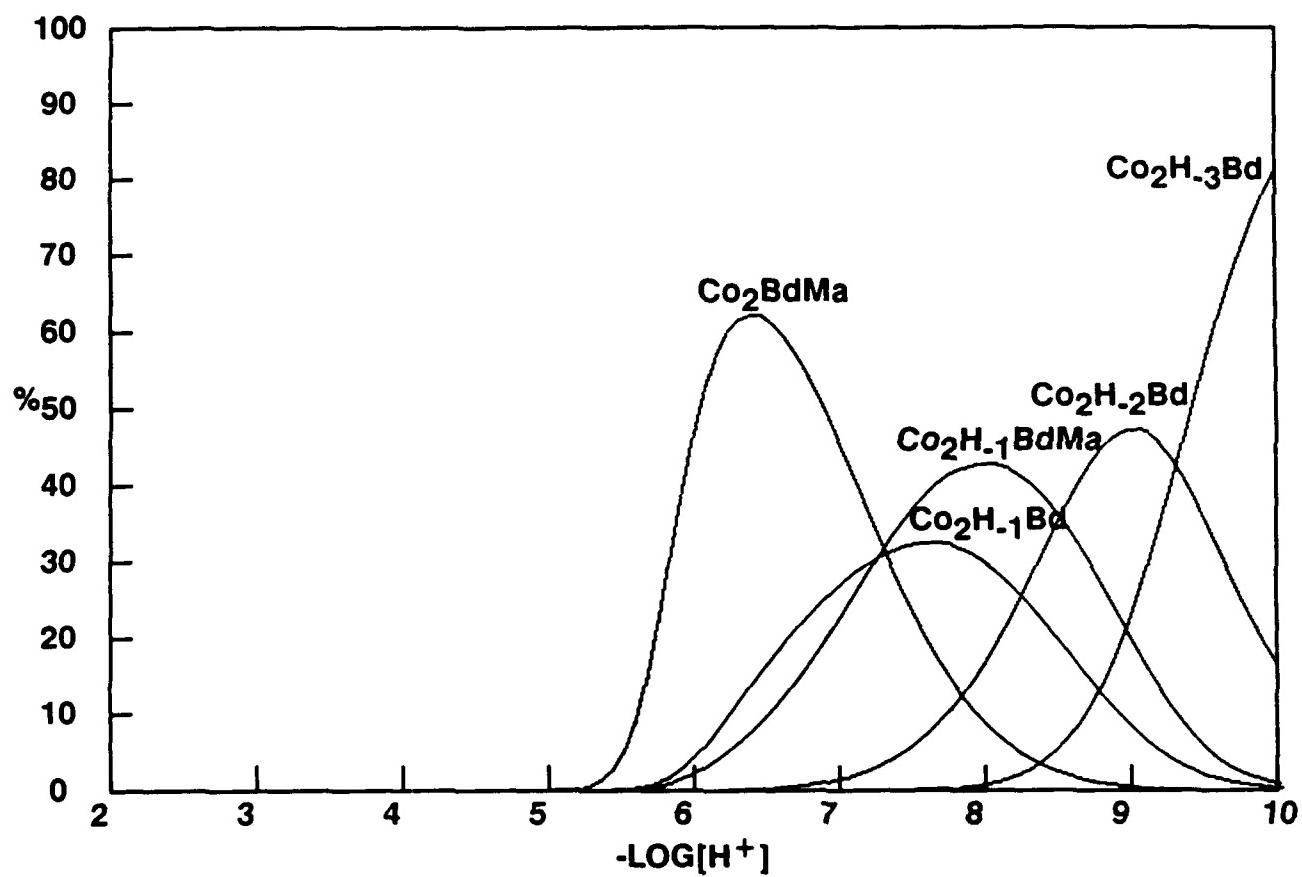
Figure 7
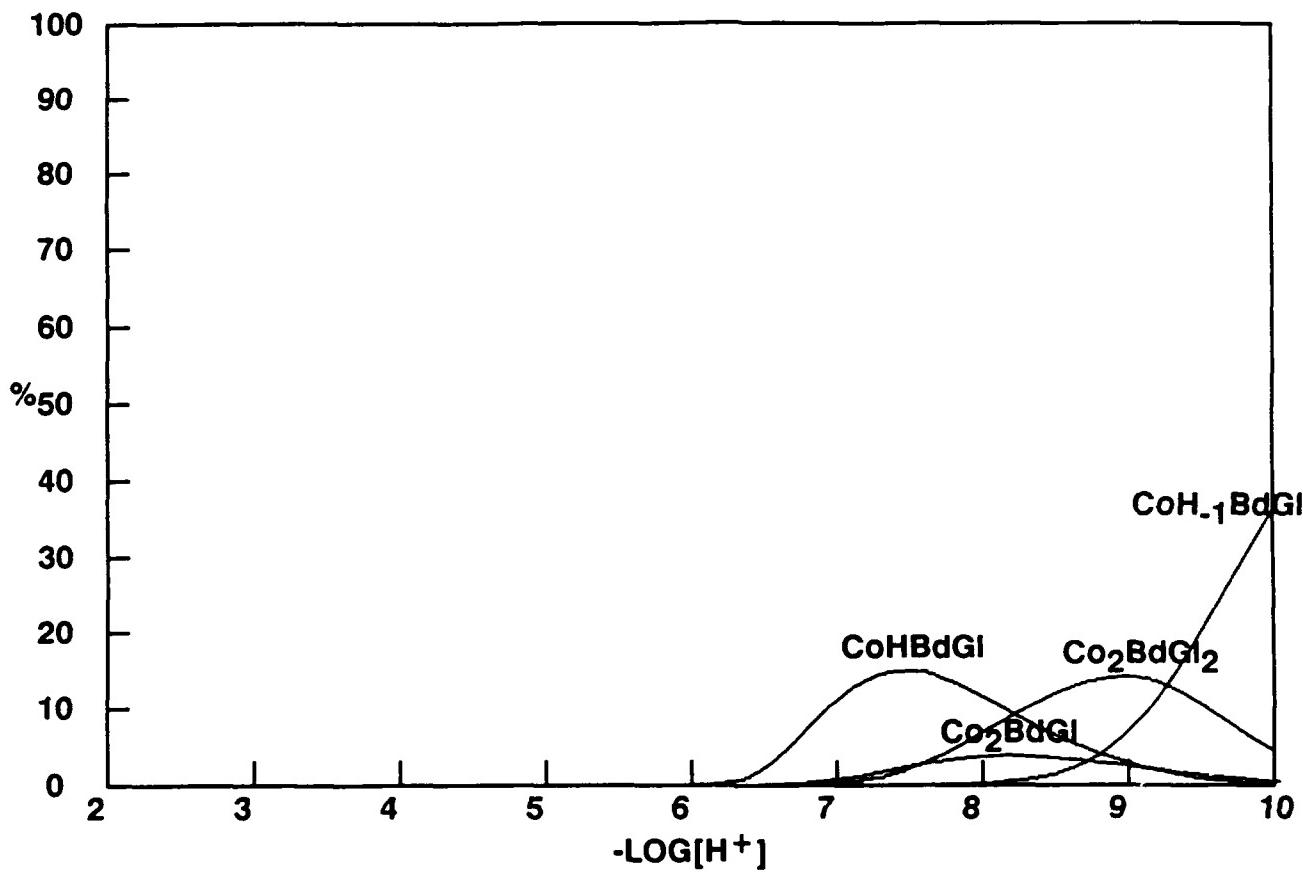
Figure 8
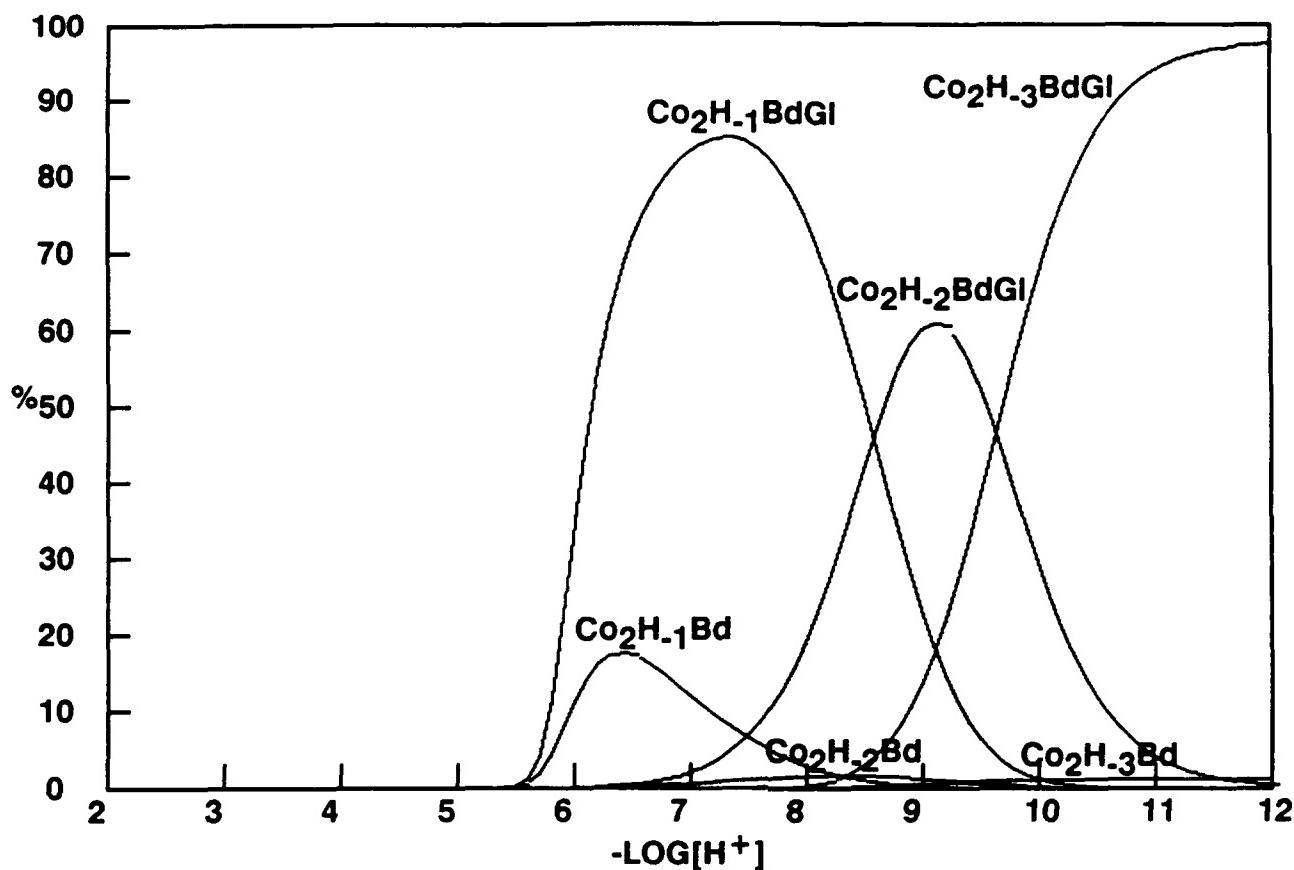
Figure 9
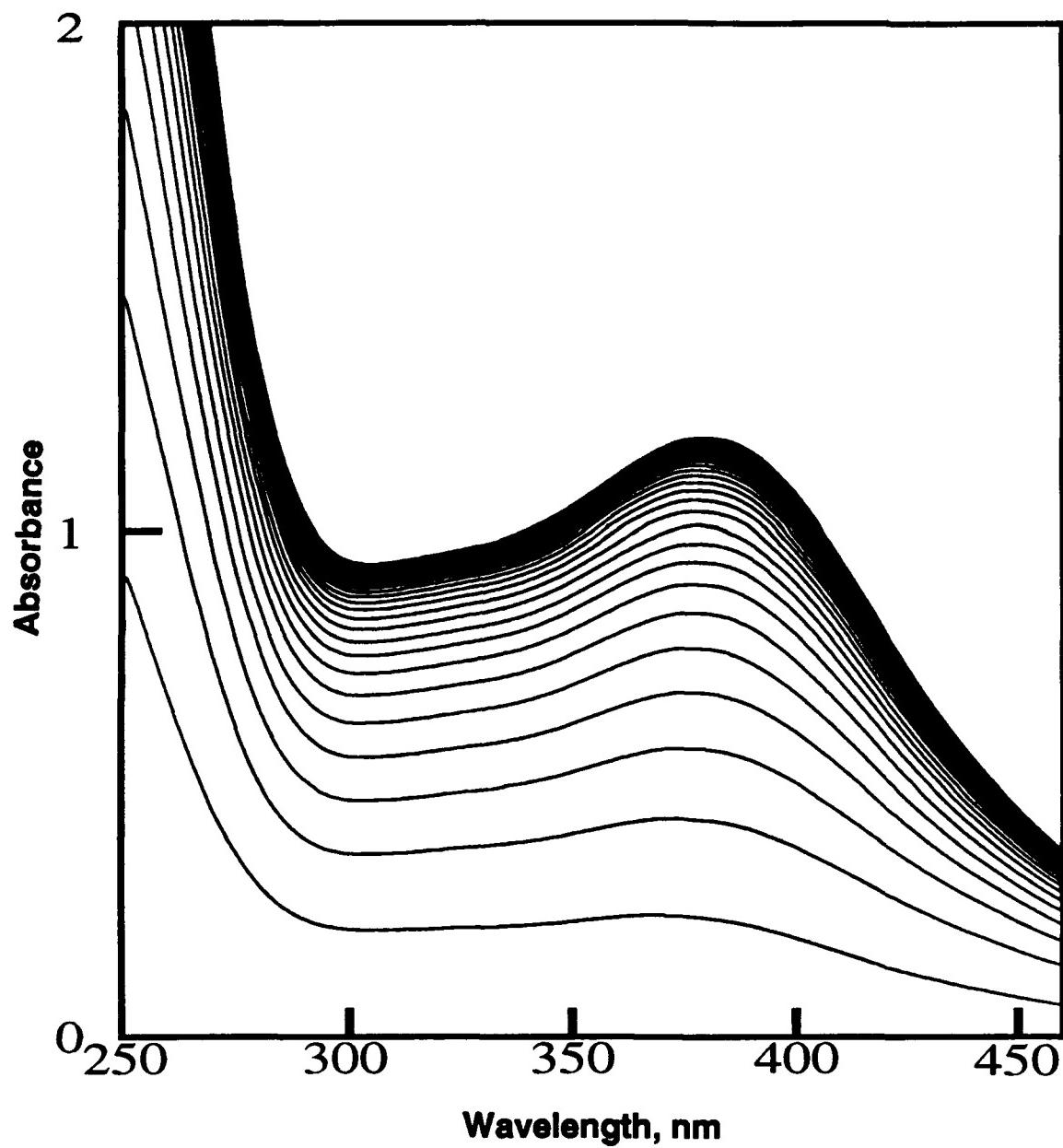
Figure 10
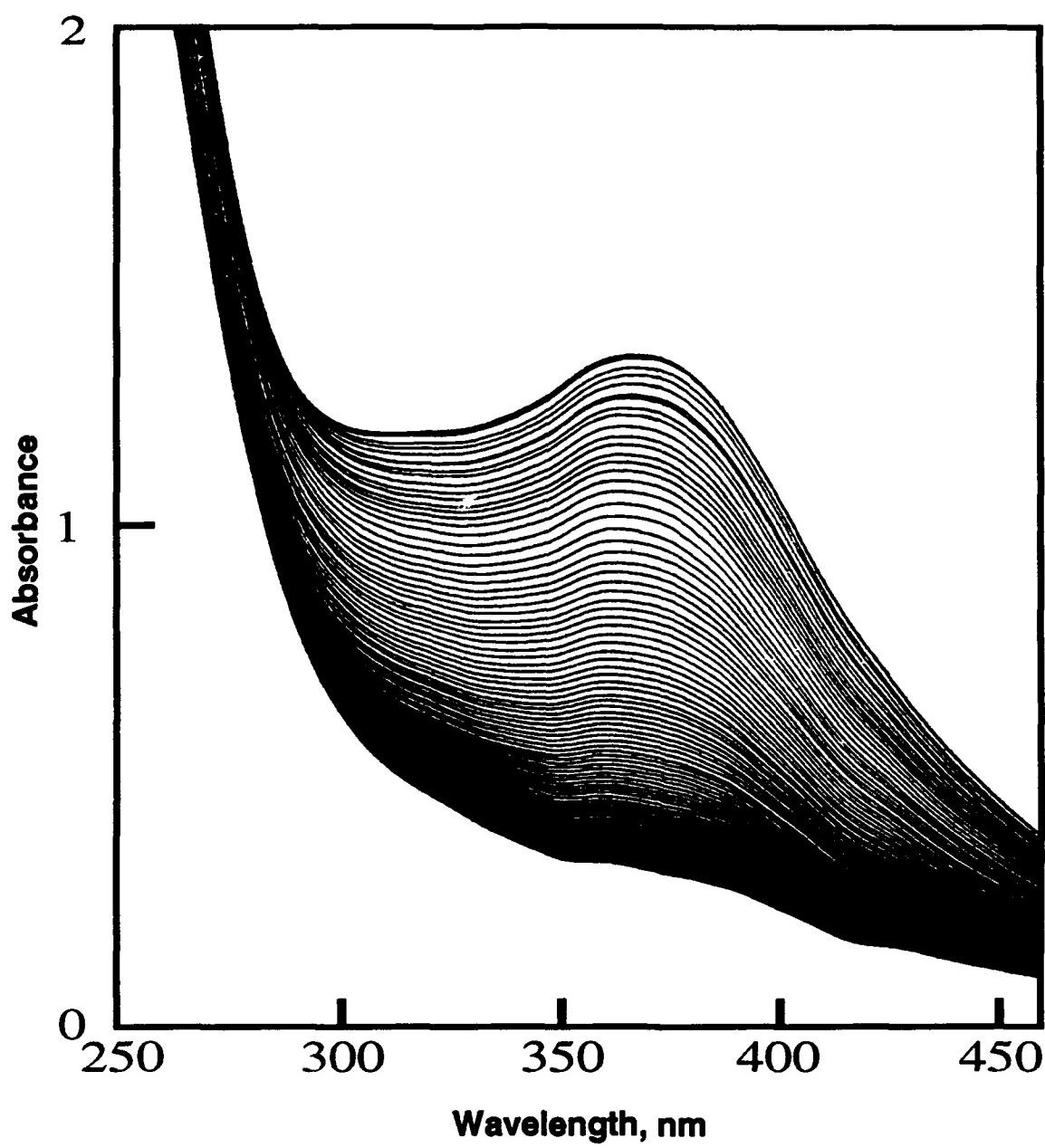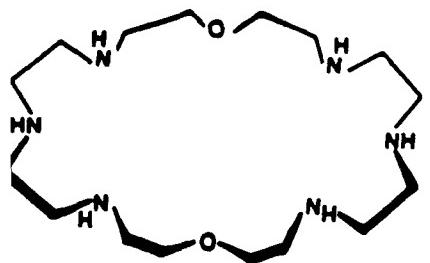
**1 O-BISDIEN**
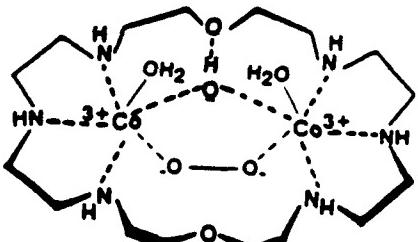
2 O-BISDIEN hydroxo-bridged dicobalt dioxygen complex
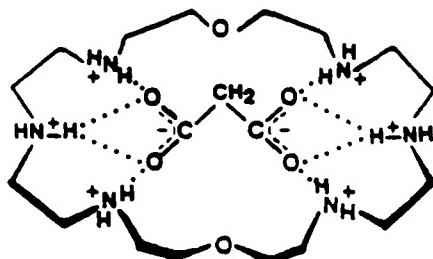
**3 Possible H-bonding modes in the complex H_6BDMal^{4+}**
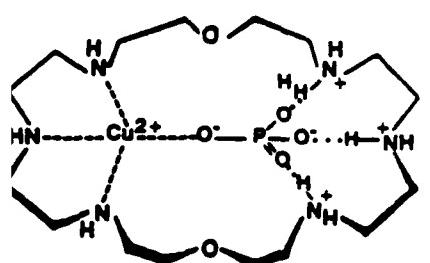
4 Possible coordinate bonding in $[Cu(HPO_4)H_3BD]^{3+}$
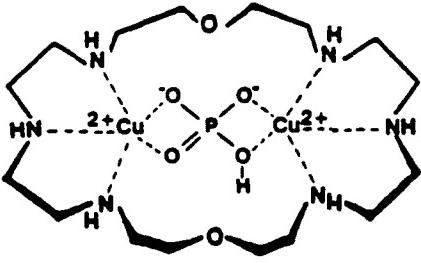
5 Possible coordindate bonding in $[Cu_2(HPO_4)BD]^{2+}$
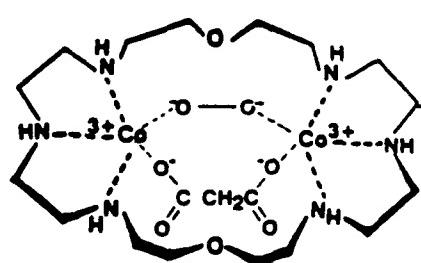
6 Suggested coordinate bonding in $[Co_2O_2(Mal)Bd]^{2+}$
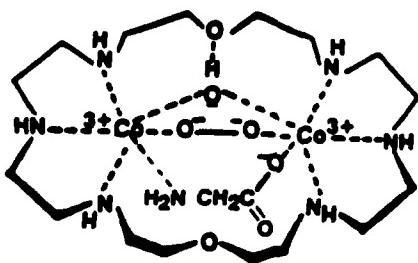
7 Suggested coordinate bonding in $[Co_2(OH)(Gly)O_2BD]^{2+}$